Journal of Environmental Chemical Engineering 12 (2024) 114026

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jece

Synthesis of biochar modified steel slag composites for passivation of multiple heavy metals in soil

An Wang, Yifan Liu, Ying Zhang, Jie Ren, Yang Zeng, Zhanbin Huang *

School of Chemical and Environmental Engineering, China University of Mining and Technology-Beijing, Beijing 100083, China

ARTICLE INFO

Keywords:
Steel slag
Biochar
Multiple heavy metals
Soil remediation
Oilseed rape cultivation

ABSTRACT

In this study, steel slag (SS) was used as the research object, and a highly efficient and environmentally friendly heavy metal passivation material (SS-BC) was synthesized using biochar (BC) as a modifier. Meanwhile, taking heavy metals lead and cadmium as examples, the study investigated the passivation ability of steel slag modified materials on lead and cadmium in soil, the improvement of soil fertility, and the impact on plant growth indicators. The results showed that in soil contaminated with heavy metals Pb and Cd, the optimal addition amount of SS-BC was 3 g/kg within 60 days, with the highest passivation efficiency of 51.76 % and 63.74 % for Pb and Cd, respectively. After treatment with SS-BC, the acid extractable fraction of heavy metals in soil significantly decreased, while the residual fraction significantly increased. The ecological risk index RI of soil contaminated with single heavy metal Cd decreased from 606.13 to 69.74. After treating various types of heavy metal contaminated soil with SS-BC, the plant height, fresh weight, dry weight, chlorophyll content, and nitrogen content of the plants significantly increased, with the plant height increasing by 58.33 %, 98.21 %, and 130.14 % compared to the CK group, and the fresh weight increasing by 157.97 %, 140.98 %, and 424.24 % compared to the CK group. Through laboratory simulation planting of rapeseed, it was found that the addition of SS-BC significantly reduced the content of heavy metals in rapeseed, while also significantly inhibiting the accumulation of heavy metals in the roots and their transfer to the leaves. After treating heavy metal contaminated soil with SS-BC, the fixation and transformation of heavy metals, improvement of soil properties, and release of nutrients were used to enhance biological activity and crop yield.

1. Introduction

In recent years, with the rapid development of industrialization, the emission of industrial and agricultural production waste, sewage irrigation, and excessive use of polluting inputs have led to the entry of various heavy metals into the soil environment [49]. The interaction of multiple heavy metals has resulted in serious soil heavy metal compound pollution problems [34]. Different degrees of heavy metal compound pollution exist in farmland, urban soil, soil around industrial sites, and mining areas, with heavy metals being transferred and enriched along the food chain, posing a great threat to human health [48]. Heavy metals in soil have characteristics such as concealment, irreversibility, and long retention time [45]. Meanwhile, the compounded pollution of multiple heavy metals exhibits increasingly severe harm, especially from heavy metals such as cadmium (Cd), lead (Pb), zinc (Zn), and mercury (Hg) with significant biological toxicity [23,50]. Among them, Cd has high mobility and biological toxicity, often causing harm to plants and human health even at low concentrations. Plant toxicity induced by Cd can inhibit plant growth, with studies showing symptoms of toxicity in peanut seedlings treated with externally added Cd, such as slow development, incomplete leaf development, and root blackening. Long-term human exposure to Cd can cause various health problems such as Itai-Itai disease, kidney failure, and neurological disorders [11,32]. Pb is one of the most documented toxic elements among known toxic elements. Pb in soil accumulates in the food chain and is transmitted to humans, where it is difficult to decompose and poses significant harm. When the accumulated intake of Pb exceeds 5 mg/kg in humans, it can cause acute poisoning, accompanied by symptoms such as headaches, hallucinations, and anemia, and can lead to death in severe cases [17]. Studies have shown that soils contaminated with heavy metal compounds not only accumulate the toxicity of individual heavy metals but also, compared to individual heavy metals, the migration, transformation, and combined toxicity of multiple heavy metals in soil are more complex and severe [18,21]. Therefore, the

* Correspondence to: Ding 11, Xueyuan Rd. Haidian D., Beijing 100083, China.
E-mail address: zbhuang202208@126.com (Z. Huang).

https://doi.org/10.1016/j.jece.2024.114026
Received 9 July 2024; Received in revised form 21 August 2024; Accepted 31 August 2024
Available online 3 September 2024
2213-3437/© 2024 Elsevier Ltd. All rights are reserved, including those for text and data mining, AI training, and similar technologies.

urgent need for comprehensive and environmentally friendly and efficient remediation technologies for heavy metal compound pollution is imminent.

Currently, various remediation techniques have been developed to address heavy metal contamination, such as the topsoil replacement method, chemical leaching, electrokinetic remediation, and stabilization/solidification techniques. Each of these methods has its unique advantages and limitations. For instance, the topsoil replacement method is costly, requires extensive engineering, and disrupts the soil's natural structure, making it suitable only for small-scale, shallow soil remediation. Chemical leaching can lead to the loss of soil organic matter and minerals, with a significant risk of secondary pollution. Although electrokinetic remediation is easy to operate and convenient to manage, it remains primarily in the experimental research stage, making large-scale field applications challenging. The solidification and stabilization technology primarily refer to the addition of exogenous amendments to alter the chemical forms of heavy metals in the soil, thereby reducing their bioavailability, and it is considered one of the most effective and low-risk remediation techniques [27]. The selection and development of green and efficient amendment products are prerequisites for the successful application of this technology, and the combined application with relevant heavy metal removal techniques is the direction for future development [5]. Chemical stabilization is considered a promising soil remediation technology due to its advantages of rapidity, simplicity, and noticeable effectiveness. This technology is relatively mature, economically practical, stable, and efficient, and is suitable for the remediation of large-scale contaminated soils [5]. In recent years, it has experienced rapid development and unprecedented attention. Some novel stabilization materials, such as biochar, ferrous sulfate clay minerals, and modified functional materials based on these materials, hold great promise in soil stabilization and remediation [7,29,30]. By developing materials with higher performance and sustainable remediation capabilities to reduce material consumption and avoid excessive remediation, while emphasizing the improvement of the long-term effectiveness of stabilization, the stabilization technology is expected to be further promoted and demonstrate new vitality in the field of soil remediation [13].

Researchers are committed to exploring more environmentally functional materials that are novel, green, economical, and efficient. In recent years, biochar has received widespread attention for its application in soil pollutant remediation globally. Biochar, a carbon-rich material, is produced from biomass (such as agricultural waste, wood, animal bones, etc.) through pyrolysis (300℃~700℃) under limited or oxygen-free conditions and has played a crucial role in controlling heavy metal pollution in controlled environments [26,28]. The physical and chemical properties of biochar, such as pH, mineral content, and surface charge, are conducive to the adsorption of oxygen cationic metals [53]. Karami et al. found that after applying biochar to Pb-contaminated soils in mining areas, the content of Pb in pore water decreased by nearly 50 % [15]. Jiang et al. reported that the acid-soluble fractions of Pb and Cu in soil decreased by 18.8~77 % and 19.7~100 %, respectively, after biochar application [12]. Furthermore, biochar has many benefits in soil improvement, such as increasing soil organic matter content, soil enzyme activity, and microbial community structure, promoting the circulation of N, P, K in soil, improving soil structure, enhancing soil fertility, water retention capacity, and carbon storage capacity [19,42]. Moreover, applying biochar helps increase arable land productivity and reduces environmental impact by substituting chemical pesticides, herbicides, and fertilizers[38]. However, as research progresses, some drawbacks of biochar are gradually emerging, such as lower adsorption efficiency for heavy metals compared to activated carbon, larger particle size, and fewer adsorption sites [3]. Additionally, the fixation of some anionic pollutants does not achieve the expected results. Therefore, to overcome these limitations, it is necessary to further activate or modify biochar to enhance its adsorption performance for multiple metals [52].

To explore the significant advantages and immense potential of biochar materials in environmental pollution control, modified applications of biochar have emerged. Modification techniques can improve the structural properties of adsorbents, such as size and particle structure, the number and volume of pores, specific surface area, and adsorption sites, thereby enhancing their adsorption capacity. Biochar modification methods include physical modification (steam, ball milling, and microwave), chemical modification (acid, alkali, and hydrogen peroxide), biological modification (digestion), and loading modification (metal salts or metal oxides, organic functional groups, and carbonaceous materials). Metal salt/metal oxide modification is commonly used as a method for biochar modification. Using metal salts or metal oxides can alter the adsorption, catalytic, magnetic properties, etc., of biochar. Common modifying metals include iron, magnesium, aluminum, manganese, etc.[16,31,51]. Chen et al. [4] found that adding MnO_2 to co-compost biochar with sediment and camellia by-products can improve the physicochemical properties of the compost, increase microbial richness and diversity, and reduce Cd and Zn by 24.72 % and 10.99 %, respectively. Yang et al.'s [47] study used broad bean straw to produce biochar, which was further modified with $FeCl_3{\cdot}6\ H_2O$ and $KMnO_4$ to obtain iron-manganese-modified biochar (FMBC) for the remediation of Cd- and Pb-contaminated soil. FMBC reduced the bioavailable concentrations of Cd and Pb by 57.51–73.73 % and 52.25–69.87 %, respectively.

Steel slag is a waste residue produced during the steelmaking process. Its low level of comprehensive utilization means that indiscriminate disposal of untreated steel slag can result in resource waste and environmental damage. Steel slag, due to its wide availability, low cost, and large specific surface area with a porous structure, containing compounds such as iron oxide and calcium oxide, can serve as an excellent adsorbent [9]. As a stable adsorbent, steel slag exhibits good adsorption effects in the treatment of industrial wastewater containing heavy metal ions, organic dye wastewater, inorganic non-metallic wastewater, and other types of industrial wastewater. Currently, the most common methods for modifying steel slag include acid modification, alkali modification, heat modification, and organic salt modification [25]. Among these, acid modification significantly reduces the leaching of metal ions from steel slag, thereby avoiding secondary pollution to the environment. It can also remove interlayer organic impurities, increase the specific surface area, and pore volume of steel slag [39]. Furthermore, acid modification can activate steel slag, enhancing its ion exchange capacity and adsorption performance [1]. Research and practical applications of steel slag have attracted significant attention from researchers in the environmental field. With the gradual depletion of mineral resources, steel slag, as a high-performance material, plays an increasingly important role in environmental governance [33,41].

In this study, a highly efficient and environmentally friendly heavy metal passivation material was synthesized by using discarded steel slag and biochar, and applied to passivate heavy metals in soil. The microstructure and elemental composition of the synthesized heavy metal passivation material were analyzed using scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and specific surface area (BET) characterization methods. Meanwhile, taking heavy metals Pb and Cd as examples, the remediation effects and mechanisms of steel slag-modified materials on Pb and Cd in soil were investigated. The impact of steel slag-modified materials on the distribution of heavy metal forms during the Pb and Cd remediation process in soil was explored. The material can not only effectively passivate heavy metals, but also enhance soil quality by improving soil fertility, enhancing cation exchange capacity, and releasing beneficial elements. Meanwhile, this study explored in detail the passivation mechanism of SS-BC on Pb and Cd, including surface adsorption, chemical complexation, cation exchange, precipitation formation and many other aspects, which provides a theoretical basis for understanding and optimising the remediation of heavy metal contaminated soil. The research results not only provide important theoretical value for the remediation of heavy

metal-contaminated soil using steel slag but also have important practical value for the development of inexpensive and efficient heavy metal remediation materials.

2. Material and methods

2.1. Preparation of SS-BC

The biochar was prepared in the laboratory. Corn stalks were crushed and placed in alumina crucibles, then pyrolyzed in a tube furnace under a nitrogen atmosphere at a heating rate of 10 °C/min for 2 hours at a pyrolysis temperature of 500°C. The steel slag used to prepare the heavy metal passivation material was purchased from Chongqing Iron & Steel Co., Ltd. Bulk steel slag was crushed and sieved through a 0.5 mm mesh to obtain steel slag powder. A measured amount of the steel slag powder was placed in a round-bottom flask, and 100 mL of 2 % sulfuric acid solution was added. The mixture was stirred in a water bath at 60°C for 30 minutes until the steel slag powder was completely dissolved and dispersed. Biochar was then added at a mass ratio of SS:BC = 5:1, and the mixture was stirred in the water bath for an additional 2 hours. After the reaction, the pH was adjusted to 7–8 using a sodium hydroxide solution of a certain concentration, followed by filtration and drying of the precipitate. Next, 15 % sodium carbonate (Na_2CO_3) was added to the dried solid product, thoroughly ground, and mixed, then placed in a tube furnace for further pyrolysis under a nitrogen atmosphere at a heating rate of 10 °C/min for 1 hour at a pyrolysis temperature of 500°C. The final product obtained was biochar-modified steel slag heavy metal passivation material (SS-BC). This method is an improvement over previous preparation methods [37]. X-ray fluorescence spectrometry (XRF) parameters of SS was listed in Table 1.

2.2. Characterization method

The instrument model and method of characterization are listed in the supplementary materials.

2.3. Soil cultivation experiments and potting experiments

Soil samples for the experiment were collected from the topsoil (0–20 cm) of farmland in Tingzizhuang Village, Changping District, Beijing. The soil had a pH of 8.17, an electrical conductivity (EC) of 144.2 μS/cm, a cation exchange capacity (CEC) of 14.37 cmol/kg, a bulk density of 1.19 g/cm^3, a field capacity of 40.0 %, an available phosphorus content of 5.61 mg/kg, an alkali-hydrolyzable nitrogen content of 14.39 mg/kg, a readily available potassium content of 270 mg/kg, and an organic matter content of 12.8 g/kg. After air-drying naturally, the soil was crushed, impurities were removed, and it was passed through a 2 mm nylon sieve.

The biochar was prepared from corn stalks by pyrolysis at 400–500℃. It had a pH of 9.8, an electrical conductivity (EC) of 956 μS/cm, a cation exchange capacity (CEC) of 20.17 cmol/kg, an organic matter content of 191.9 g/kg, and contained 15.82 % carbon, 1.07 % hydrogen, 7.75 % oxygen, 0.28 % nitrogen, and 0.26 % sulfur. The biochar was passed through an 80-mesh nylon sieve and set aside for use.

Take the prepared soil and add $Pb(NO_3)_2$ and $Cd(NO_3)_2$ solutions, mixing thoroughly to create contaminated soils. Specifically, prepare lead-contaminated soil at a concentration of 500 mg/kg by adding 1 L of 5 g/L $Pb(NO_3)_2$ solution to every 10 kg of soil, and cadmium-contaminated soil at a concentration of 100 mg/kg by adding 1 L of 1 g/L $Cd(NO_3)_2$ solution to every 10 kg of soil. Maintain the soil moisture content at 25 %, allow the contaminated soils to stabilize and age for one month, then air-dry them naturally, and pass them through a 2 mm sieve for later use. To ensure the stability and consistency of the soil's physicochemical properties, the lead-cadmium mixed contaminated soil was prepared by mixing equal amounts of the single contaminated soils.

In the soil cultivation experiment, 500 g of each of the three types of heavy metal-contaminated soil was weighed into pots. Different proportions of SS and SS-BC (0.1 %, 0.2 %, 0.3 %, 0.4 %, and 0.5 %) were added to each of the three types of heavy metal-contaminated soil. Soil without any additives was used as the control group. Periodically, deionized water was applied to maintain soil moisture content at 20 % [40,56]. The pots were placed in a constant temperature incubator at 25°C for 60 days. Destructive sampling was conducted at 10, 20, 30, and 40 days to analyze soil chemical indicators, the content of available lead, and the distribution of lead in different forms in the soil. The heavy metal passivation efficiency is calculated as follows:

$$P = \frac{E_s}{E_{CK}} \times 100\%$$

Where, P is the passivation efficiency of heavy metals, %; E_{CK} is the effective state content of heavy metals in the blank control group, mg/kg; E_s is the effective state content of heavy metals in the experimental group, mg/kg.

In the pot experiment, urea and potassium dihydrogen phosphate were added to the three types of heavy metal-contaminated soil at proportions of 0.20 g/kg and 0.36 g/kg, respectively, and thoroughly mixed. For each treatment, 0.30 % of the material was mixed with 500 g of contaminated soil, placed into plastic pots with holes in the bottom and lined with a layer of filter paper. Each treatment was replicated three times. Water was added to adjust the soil moisture content to 80 % of field capacity, and after aging for one week, seeds were sown. Fifteen full seeds of Oilseed Rape were evenly spread in each pot, and after seven days of seedling emergence, thinning was performed, leaving five evenly distributed and similarly growing seedlings in each pot. During the growth period, watering was done as needed to keep the soil consistently moist. Upon maturity, the Oilseed Rape was harvested and taken back to the laboratory. Growth parameters such as leaf length, leaf width, and plant height were measured, and the above-ground and below-ground dry and fresh weights of the Oilseed Rape were recorded. The heavy metal content in both above-ground and below-ground parts of the Oilseed Rape was determined. A portion of the harvested potting soil samples was air-dried naturally, sieved through a 1 mm mesh, and used to analyze soil physicochemical properties as well as the content of available and different forms of heavy metals in the soil.

3. Results and discussion

3.1. Characteristics of prepared SS-BC and SS

Fig. 1 (A-B) respectively show the scanning electron microscope images of SS and SS-BC at 2.00 μm. It can be seen from the figures that SS exhibits irregular block-like structures, with a rough surface and a large number of particles attached. The surface granularity of SS-BC is finer, and the sediment distribution is more uniform. Upon careful

Table 1
XRF detection of relative content of elements in SS.

atomic	O	Ca	Fe	Si	Mg	Al	Mn	Ti	P	else
intensities	/	687.01	728.02	472.65	53.12	165.95	59.77	5.67	57.36	/
Mass/%	44.96	23.03	11.93	8.70	3.51	3.38	1.59	0.71	0.59	1.6

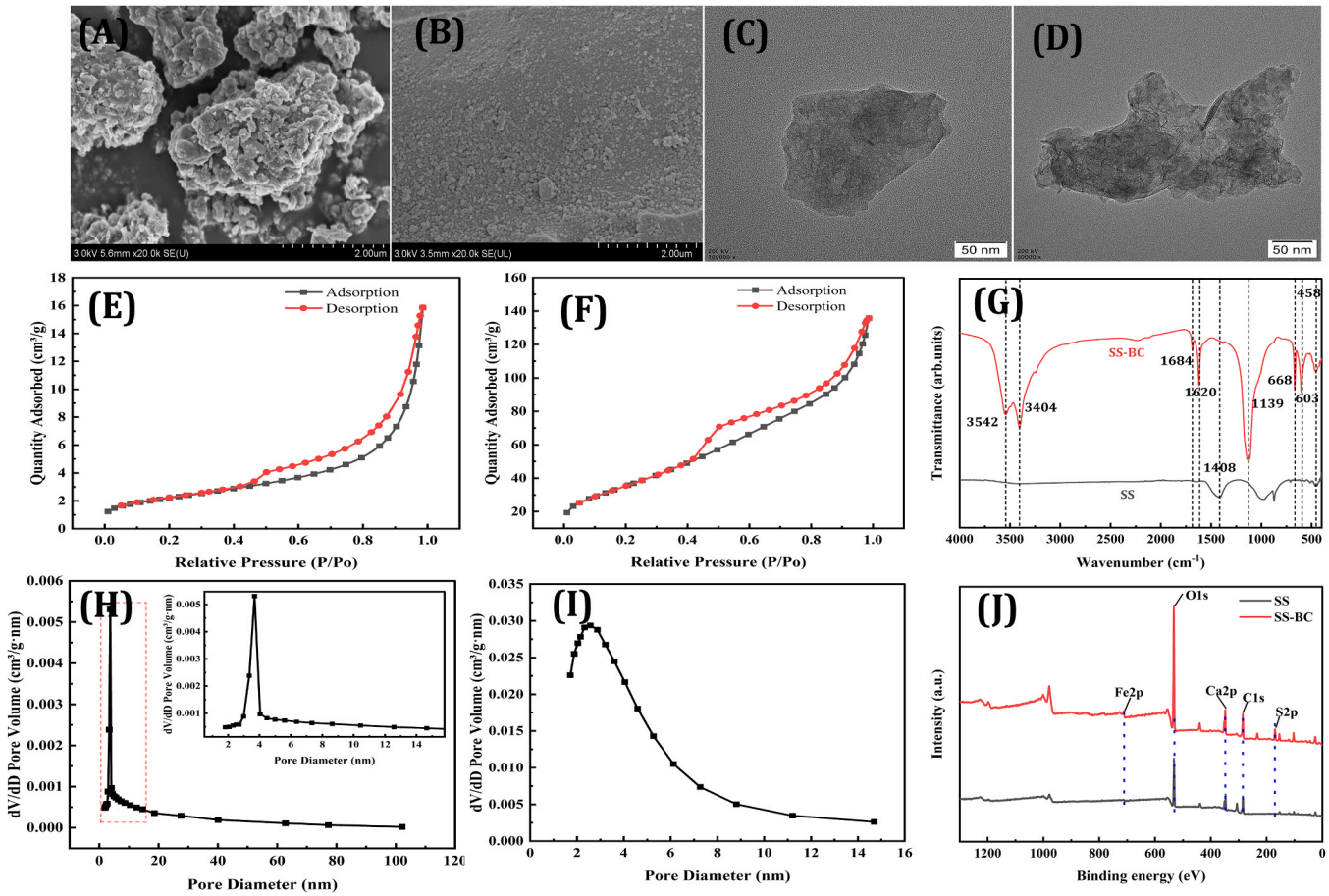

Fig. 1. SEM patterns of SS (A) and SS-BC (B), TEM patterns of SS (C) and SS-BC (D), N2 adsorption-desorption curves of SS (E) and SS-BC (F), FT-IR patterns (G) of SS and SS-BC, pore size distributions of SS (H) and SS-BC (I), and XPS (J) patterns of SS and SS-BC.

observation, fine cracks and pores can be found. Meanwhile, in Fig. 1 (C-D), under the same magnification, the interior of SS appears thick and compact, forming a complete block-like particle solid. However, numerous pore channels can be clearly observed in the interior of SS-BC. During the preparation of SS-BC, a large amount of calcium iron oxide in SS is eroded and deposited on the surface of biochar, leaving behind numerous pores on the surface of biochar, which is also the reason for its increased specific surface area [36].

The N_2 adsorption-desorption curves of SS and SS-BC are shown in Fig. 1 (E, F), respectively, from which it can be seen that the inflection point occurs at relative pressure greater than 0.5 and the curve is concave, so the adsorption curves belong to type IV adsorption curves in IUPAC classification. Not only that, the adsorption curve of SS-BC has an H3 hysteresis loop, which indicates the result of a large amount of N_2 aggregation in the pores in the range of medium pressure, which proves that SS-BC belongs to mesoporous materials. Fig. 1(H, I) shows the pore size distribution curves of SS and SS-BC, respectively, and it can be seen that the specific surface area of SS-BC increases dramatically, which may be a result of the erosion of the surface of the biochar by a large amount of iron and calcium oxides in the steel slag. The specific parameters of BET are listed in Table 2. Fig. 1(G) shows the infrared spectra of SS and SS-BC, in which the telescopic vibration peaks located at 3542 cm^{-1} and 3404 cm^{-1} should be the free -OH, the telescopic vibration peak of unsaturated -C═C at 1684 cm^{-1}, the telescopic vibration peak of -C═O at 1620 cm^{-1}, and the peak at 1139 cm^{-1} is the telescopic vibration peak related to the -C-OH in the aliphatic hydrocarbon [6,43]. Overall, it seems that the activated functional groups of the SS-BC material increased substantially after modification, which is favorable for the adsorption and immobilization of heavy metals. The XPS gross spectra on SS and SS-BC in Fig. 1(J) also show that elements such as Fe, Ca in steel slag were also successfully loaded onto the surface of biochar [35].

Table 2
BET data parameters for SS and SS-BC.

Pore characteristics	SS	SS-BC
BET surface area (m^2/g)	3.8584	181.7329
Average pore volume (cm^3/g)	0.0224	0.0682
Average pore size (nm)	23.2626	2.8798

3.2. *Effect of steel slag modified materials on heavy metals remediation in soil*

3.2.1. *Effect of steel slag modified materials on the physicochemical properties of soil*

The occurrence forms of heavy metals in soil are closely related to chemical indicators such as soil organic matter, CEC, pH value, and electrical conductivity. Generally, the toxicity of heavy metals varies with changes in the physicochemical properties of the soil [22,55]. The physicochemical indicators of different soils after treatment with SS-BC for various heavy metal pollution are shown in Fig. 2. Studies have shown that soil pH can affect the adsorption-desorption, precipitation, and migration processes of heavy metals Pb and Cd, thereby influencing the occurrence forms of heavy metals in soil [54]. As shown in Fig. 2 (A), it can be seen that SS-BC can effectively increase the pH of different heavy metal-contaminated soils. This is mainly because the calcium iron hydroxide in SS-BC hydrolyzes to produce a large amount of free hydroxyl ions in the soil, which is a key factor in increasing soil pH. Soil

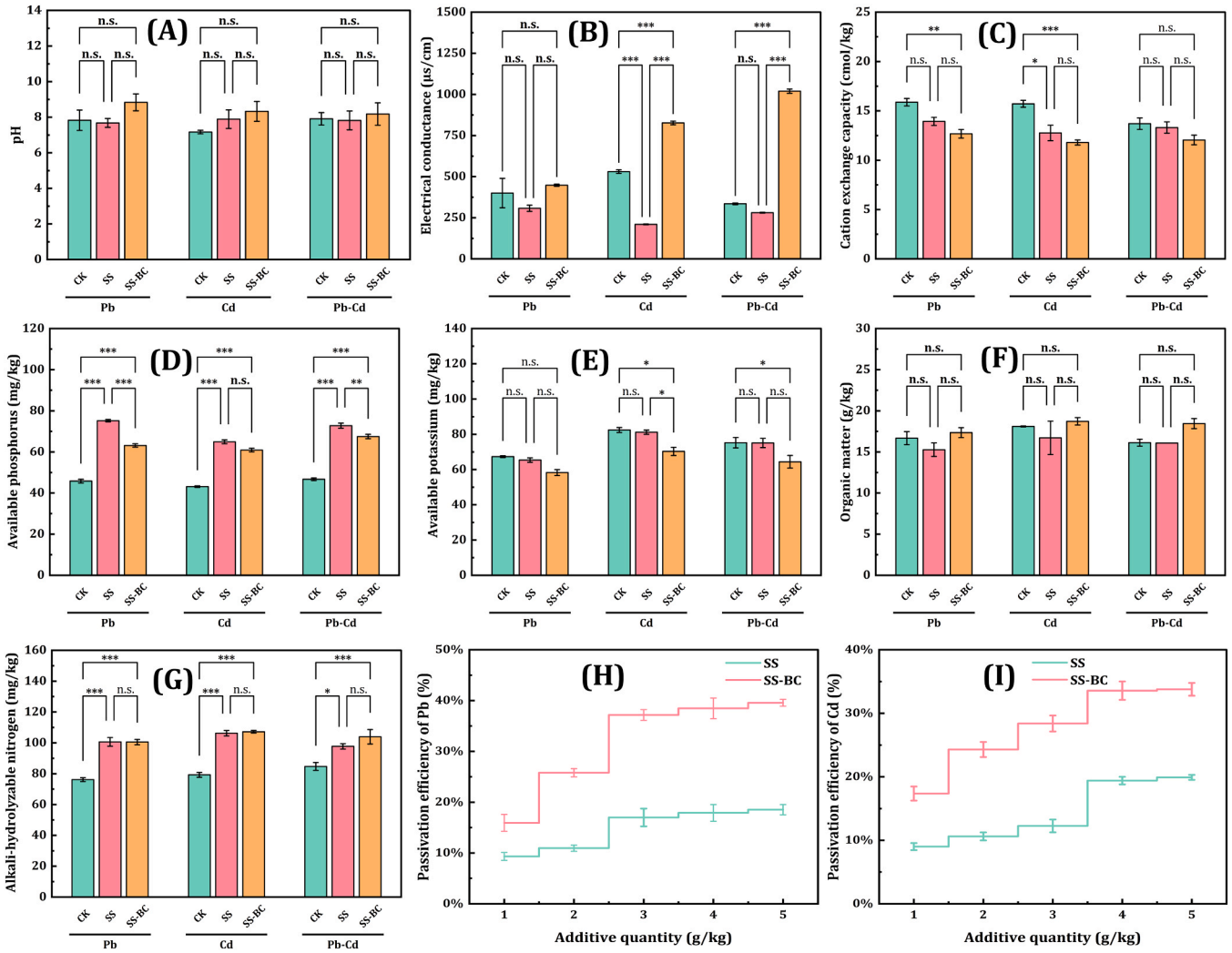

Fig. 2. Physicochemical indicators of soil after treatment of different heavy metal-contaminated soils by SS and SS-BC: pH (A), electrical conductivity (B), cation exchange capacity (C), available phosphorus (D), available potassium (E), organic matter (F), alkali-hydrolyzable nitrogen (G); Effect of addition amount on heavy metal passivation efficiency: Pb (H), Cd (I). Where $p \leq 0.05$ is generally significant, denoted as *; $p \leq 0.01$ is significant, denoted as **; $p \leq 0.001$ is highly significant, denoted as ***.

electrical conductivity can be used to quantitatively determine soluble substances such as cations and anions, and there is a positive correlation between them. As shown in Fig. 2 (B), after cultivating for 40 days with the addition of SS-BC in soils contaminated with different types of heavy metals, the electrical conductivity was significantly higher than that of the CK group. This is because the increase in soluble ions such as $Ca^{2+}$and Fe^{3+} in the soil after adding SS-BC is conducive to ion exchange with Pb (II) and Cd (II) in the soil, thereby increasing the soil electrical conductivity. However, the reason for the decrease in electrical conductivity in heavy metal-contaminated soils after adding untreated SS is that the large amount of metal oxides contained in the steel slag cannot hydrolyze in the soil, thus failing to produce soluble ions. This leads to soil compaction and calcification, which is not conducive to ion exchange. The changes in soil cation exchange capacity (CEC) after the application of SS and SS-BC are shown in Fig. 2 (C). As can be seen from the figure, the CEC shows a decreasing trend. On one hand, Both SS and SS-BC contain alkali metal and alkaline earth metal ions, such as Ca^{2+}, Mg^{2+}, and K^{+}. However, due to the treatment process, SS-BC makes these ions more readily exchangeable, leading to increased competition for cation exchange sites in the soil. This can result in the displacement of beneficial cations originally adsorbed at these sites, potentially reducing the soil's cation exchange capacity (CEC). On the other hand, the alkaline substances in SS and SS-BC can promote the precipitation and fixation of certain heavy metals, reducing their activity in the soil solution. While this helps reduce the toxicity of heavy metals, it may also occupy cation exchange sites, thereby decreasing the CEC [20].

Nitrogen, phosphorus, and potassium are the three primary nutrients essential for plant growth. Proper application of N, P, and K fertilizers can significantly improve soil fertility, promote healthy plant growth, and increase crop yield and quality [14,46]. As shown in Fig. 2 (D), the application of SS and SS-BC significantly increased the available phosphorus content in the soil. This is because steel slag typically contains a certain amount of phosphorus compounds. After the application of SS and SS-BC, these phosphorus compounds gradually release into the soil, increasing the available phosphorus content. Additionally, the calcium and magnesium ions in the materials can react with soil phosphates to form more soluble phosphate compounds, thus enhancing phosphorus availability. The presence of calcium and magnesium ions also inhibits the activity of iron and aluminum ions, reducing phosphorus fixation. From Fig. 2 (E), it can be observed that the addition of SS and SS-BC decreases the available potassium content in the soil. This occurs because the increased concentration of calcium and magnesium ions from SS and SS-BC competes with potassium ions for adsorption sites on soil colloids. Due to their higher valence, calcium and magnesium ions have a stronger competitive ability, displacing potassium ions, which then enter the soil solution and are subsequently leached or fixed,

reducing the available potassium content. Similarly, the application of SS also reduces the soil organic matter content, as shown in Fig. 2 (F). This is because the alkaline substances such as calcium and magnesium in steel slag may react with organic acids in the soil, forming insoluble salts and thereby reducing the effective organic matter content. In contrast, the application of SS-BC increases the soil organic matter content, possibly because biochar-modified steel slag enhances its organic carbon content. The addition of SS-BC can directly increase the soil organic matter content. Fig. 2 (G) indicates that the addition of SS and SS-BC can significantly increase the soil alkaline hydrolyzable nitrogen content. On one hand, SS usually has an alkaline nature, which, when applied to the soil, raises the soil pH. A higher pH environment helps reduce ammonia volatilization losses, increases nitrogen availability, and promotes the mineralization and release of nitrogen in the soil, thereby increasing the alkaline hydrolyzable nitrogen content. On the other hand, SS-BC contains numerous hydroxyl, carboxyl, and other acidic oxygen-containing functional groups with a high negative charge density. These can adsorb alkaline hydrolyzable nitrogen through electrostatic attraction, achieving nitrogen retention.

3.2.2. *Effect of heavy metal passivation in soil of steel slag modified materials*

Fig. 2 (H, I) shows the effect of the addition of SS and SS-BC on the passivation efficiency of heavy metals Pb and Cd. The passivation rates of Pb and Cd in the soil by SS and SS-BC increased with the addition amount and tended to stabilize. When the addition amount of SS and SS-BC was 3 g/kg, the passivation efficiency of Pb reached the highest values of 18.52 % and 39.57 %, respectively, and then tended to stabilize. When the addition amount of SS and SS-BC was 4 g/kg, the passivation efficiency of Cd reached the highest values of 19.91 % and 37.78 %, respectively, and then tended to stabilize. The addition of SS-BC significantly reduced the mobility and bioavailability of Pb and Cd in the soil, thereby reducing environmental hazards. This is mainly because SS-BC has a larger specific surface area and a more porous structure compared to SS, which provides it with a strong adsorption capacity for heavy metal ions. Through physical and chemical adsorption, heavy metal ions can be firmly fixed on the surface and pores of steel slag and biochar, reducing their concentration and mobility in the soil solution. To more intuitively summarize the passivation effects of SS and SS-BC on Pb and Cd in the soil, and considering factors such as raw material costs and the passivation effects on Pb and Cd in the soil, 4 g/kg was chosen as the optimal addition amount for SS and SS-BC in subsequent experiments.

Research on the effect of different time periods on the passivation efficiency of heavy metals in soil reveals that for all types of heavy metal pollution, the passivation efficiency increases over time. Fig. 3 (A, E) show the trend of passivation efficiency and available state content over time for soil contaminated with a single heavy metal, Pb. It can be observed that after 60 days, the passivation rate of Pb reached 48.92 %, and the available state content of Pb was 255.40 mg/kg. Compared to the CK and SS groups, the available state content of Pb decreased by 71.60 mg/kg and 50.40 mg/kg, respectively. Fig. 3 (B, F) show the trend of passivation efficiency and available state content over time for soil contaminated with a single heavy metal, Cd. It can be observed that after 60 days, the passivation rate of Cd reached 57.28 %, and the available state content of Cd was 42.72 mg/kg. Compared to the CK and SS groups, the available state content of Cd decreased by 17.06 mg/kg and 8.96 mg/kg, respectively. Fig. 3 (C, G) and Fig. 3 (D, H) show the trends

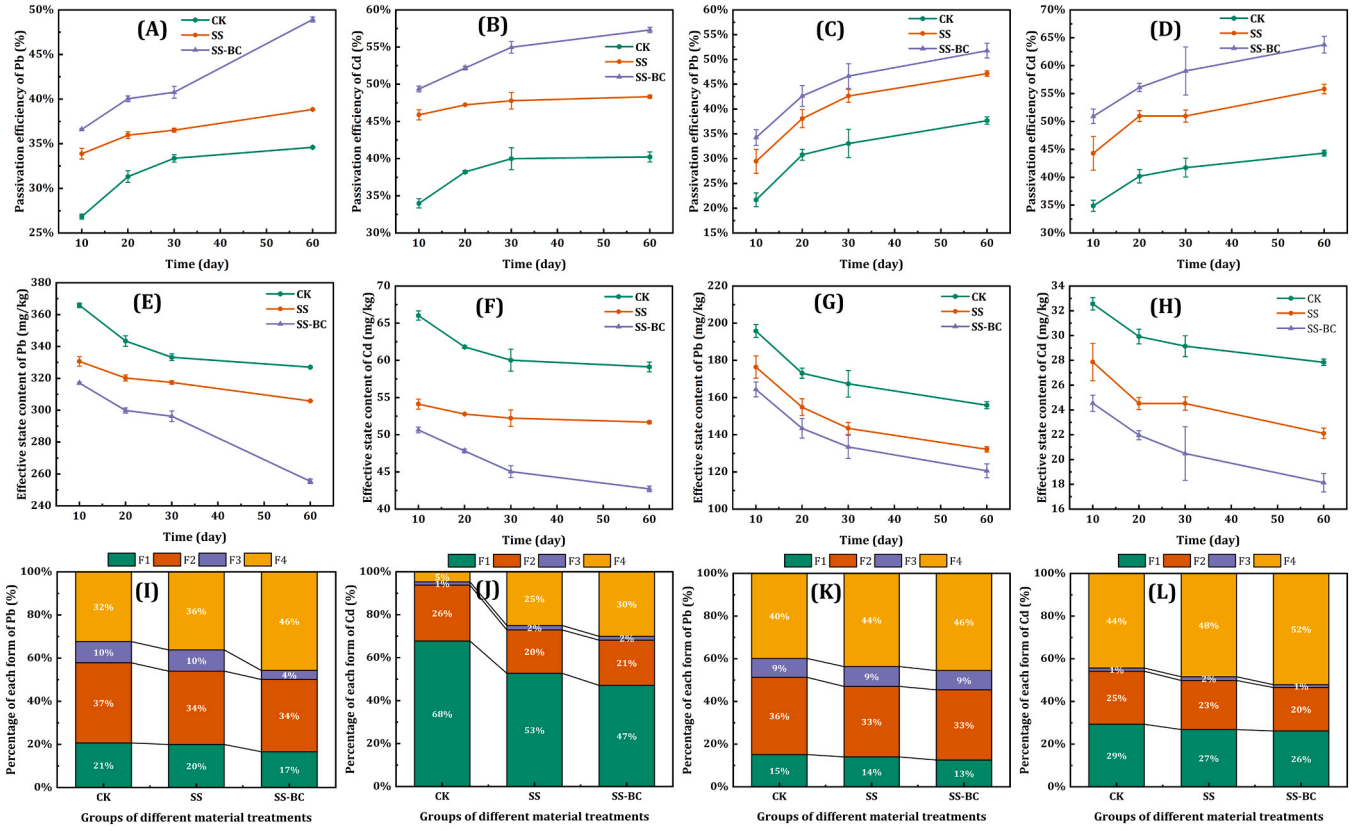

Fig. 3. Passivation efficiency of heavy metals in soils with different types of heavy metal pollution after the addition of steel slag-modified materials: single Pb pollution (A), single Cd pollution (B), combined Pb and Cd pollution (C, D); available heavy metal content in soils with different types of heavy metal pollution after the addition of steel slag-modified materials: single Pb pollution (E), single Cd pollution (F), combined Pb and Cd pollution (G, H); heavy metal speciation distribution in soils with different types of heavy metal pollution after the addition of steel slag-modified materials: single Pb pollution (I), single Cd pollution (J), combined Pb and Cd pollution (K, L).

of passivation efficiency and available state content over time for soil contaminated with mixed heavy metals Pb and Cd. It can be observed that after 60 days, the passivation rate of Pb reached 51.76 %, and the passivation rate of Cd reached 63.74 %. The mineral components in the modified steel slag, such as calcium oxide and magnesium oxide, also have good adsorption properties, allowing them to undergo physical and chemical adsorption with heavy metal ions. Additionally, the modified SS-BC contains a large number of functional groups, such as carboxyl and phenolic hydroxyl groups, which can exchange ions with heavy metal ions in the soil, thereby immobilizing the heavy metals. Analysis of the data reveals that the passivation efficiency of heavy metals in soils with mixed heavy metal pollution is higher than that in soils with single heavy metal pollution. This may be due to a synergistic adsorption effect between different heavy metals. Pb and Cd can alter the chemical environment on the surface of the adsorbent, thereby enhancing the adsorption capacity for the other heavy metal. For example, the presence of one heavy metal may promote the co-precipitation or complexation of another heavy metal, thereby increasing the overall passivation effect [2,24].

The distribution of different forms of heavy metals in soil was determined using the BCR sequential extraction method. The heavy metal forms include acid-extractable (F1), reducible (F2), oxidizable (F3), and residual (F4). The mobility of heavy metals in soil can be assessed by the absolute and relative contents of the weakly bound fractions [8,57]. The formula for calculating the migration coefficient of heavy metals in soil is as follows:

$$MF = \frac{F1}{F1 + F2 + F3 + F4} * 100 \quad (1)$$

Where F1 represents the concentration of acid-extractable heavy metals in the soil, F2 represents the concentration of reducible heavy metals in the soil, F3 represents the concentration of oxidizable heavy metals in the soil, and F4 represents the concentration of residual heavy metals in the soil [44].

$$C_f = \frac{C_i}{C_n} \quad (2)$$

$$E_r = T_r \times C_f \quad (3)$$

$$RI = \sum E_r \quad (4)$$

Where C_i represents the concentration of extractable heavy metals (F1+F2+F3); C_n represents the concentration of residual heavy metals (F4); C_f represents the heavy metal pollution coefficient; T_r represents the toxicity response coefficient of heavy metals, with Pb being 5.0 and Cd being 30; E_r represents the potential ecological risk index of heavy metals; and RI denotes the total potential ecological risk index of the soil after adding SS-BC [10].

To better elucidate the remediation effects of steel slag-modified materials on soil heavy metals and reveal the mechanisms of these materials in soil heavy metal remediation, the BCR sequential extraction method was employed to study the transformation patterns of Pb and Cd in soil treated with SS-BC. The distribution of heavy metal forms in the soil is shown in Fig. 3 (I-L). After treatment with steel slag-modified materials, the acid-extractable fraction of heavy metals significantly decreased, while the residual fraction increased. In soils with single heavy metal contamination, the acid-extractable fractions of Pb and Cd decreased by 4.07 % and 20.64 %, respectively, while the residual fractions of Pb and Cd increased by 13.41 % and 25.36 %, respectively, after adding SS-BC. Similarly, in soils with mixed heavy metal contamination, the acid-extractable fractions of Pb and Cd decreased by 2.56 % and 3.13 %, respectively, while the residual fractions of Pb and Cd increased by 5.71 % and 7.80 %, respectively, after adding SS-BC. This is mainly because SS-BC contains abundant active functional groups that facilitate complexation reactions with Pb and Cd, and it also contains calcium and magnesium oxides. The alkalinity of these oxides promotes the transformation of free Pb and Cd into insoluble precipitates, thereby reducing the mobility of heavy metals.

The migration coefficients (MF) of heavy metals in different types of contaminated soils treated with SS-BC are shown in Table 3. Refer to Table S1 of the Grading Criteria for Potential Ecological Risk Factors and Potential Ecological Risk Indices. It can be observed that, compared to the CK group, the migration coefficients of heavy metals in various contaminated soils significantly decreased after SS-BC treatment. In soil contaminated with single heavy metal Pb, the total potential ecological risk index (RI) decreased from 10.45 to 5.9 after SS-BC treatment, where RI<50 indicates a low pollution level. This directly demonstrates that the addition of SS-BC can improve the stability of heavy metals in the soil. In soil contaminated with single heavy metal Cd, the total potential ecological risk index decreased from 606.13 to 69.74 after SS-BC treatment, where RI>200 indicates a very high pollution level, and 50<RI<100 indicates a moderate pollution level. In soil contaminated with mixed heavy metals Pb and Cd, the total potential ecological risk index decreased from 45.18 to 33.50 after SS-BC treatment, indicating that SS-BC more effectively immobilizes heavy metals in mixed contamination scenarios. The interaction between heavy metal ions enhances the passivation capacity of SS-BC for heavy metals.

3.2.3. Passivation mechanism of heavy metals in soil

The addition of biochar-modified steel slag (SS-BC) to heavy metal Pb and Cd contaminated soils can effectively reduce the effective state content of heavy metals in the soil through a series of physicochemical actions. The process is summarised and explained in detail below: (I) Surface adsorption and complexation reaction: SS-BC has a rich pore structure and a large number of surface functional groups, such as hydroxyl (-OH) and carboxyl (-COOH) groups, which are able to undergo adsorption and complexation reactions with heavy metal ions, such as Pb^{2+} and Cd^{2+}. These reactions reduce the free ionic form of the heavy metals, thereby reducing their mobility and bioavailability in the soil. (II) pH enhancement: SS-BC is usually alkaline in nature and when added to the soil it raises the pH of the soil. Higher pH encourages the formation of hydroxide or carbonate precipitates from heavy metal ions such as Pb^{2+} and Cd^{2+}, which are less soluble, thereby reducing the solubility of heavy metals in the soil. (III) Increased cation exchange capacity: Cations such as calcium, magnesium and iron contained in biochar and steel slag can exchange ions with Pb^{2+} and Cd^{2+} in the soil. This process enhances the cation exchange capacity of the soil so that heavy metal ions are immobilised on the surface of the soil colloid, reducing their bioavailability. (IV) Formation of stabilising compounds: Silicates and phosphates in SS-BC react with Pb^{2+} and Cd^{2+} to form stable metal silicates or phosphates. These compounds are structurally stable and not easily soluble, thus reducing the mobility and bioavailability of heavy metals. (V) Microencapsulation and macrofixation: SS-BC not only reduces the effective state content of heavy metals through chemical reaction, but also encapsulates heavy metals in its porous structure

Table 3
Pollution factors and risk indices of different types of contaminated soils after soil cultivation experiments.

Contamination type	Treatment	MF	C_f	E_r	RI (SS-BC)
single Pb	CK	20.63	2.09	10.45	5.90
	SS	19.92	1.76	8.81	
	SS-BC	16.56	1.18	5.9	
single Cd	CK	67.76	20.20	606.13	69.74
	SS	52.72	2.99	89.82	
	SS-BC	47.12	2.32	69.74	
Mix Pb	CK	15.08	1.50	7.54	33.50
	SS	14.00	1.29	6.45	
	SS-BC	12.52	1.19	5.97	
Mix Cd	CK	29.30	1.25	37.64	
	SS	26.83	1.06	31.94	
	SS-BC	26.17	0.91	27.53	

through microencapsulation. At the same time, it can also promote the macro fixation effect of soil, so that the mobility of heavy metals in the soil is greatly reduced. (VI) Improvement of soil fertility: SS-BC also improves soil structure and fertility by releasing beneficial minerals and nutrients (e.g. Ca^{2+}, Mg^{2+}, etc.). These effects not only help to reduce the toxicity of heavy metals, but also promote plant growth and improve the biological activity of the soil.

3.3. Effect of steel slag modified materials on bioavailability in heavy metal contaminated soil

3.3.1 Assessment of the impact of planting rapeseed in soil treated with steel slag modified material on soil physicochemical parameters in heavy metal contaminated soil

Fig. 4(A) shows the effect of adding SS-BC to soils contaminated with different types of heavy metals on pH values. It can be seen that the improvement in soil pH with SS-BC is very significant. This is mainly because SS-BC contains abundant CaO, which reacts with CO_2 and H_2O to form alkaline oxides, thereby reducing the H^+ content in the soil. Additionally, the rich Fe content in SS-BC can react with hydroxide ions in the soil to form insoluble iron hydroxides, which precipitate out of solution. This process reduces the concentration of free H^+ ions, thereby increasing the soil pH. Silicon in SS-BC, typically present as silicates, may slowly weather and release silicic acid, but this process generally does not directly impact the formation of insoluble compounds with H^+. Fig. 4(B, C) show the effects of adding SS-BC to soils contaminated with different types of heavy metals on electrical conductivity and cation exchange capacity. It can be seen that the soil electrical conductivity increases significantly after adding SS-BC, while the cation exchange capacity decreases slightly but not significantly. This is because SS-BC contains a certain amount of soluble salts and ions (such as calcium and magnesium ions). When these ions are added to the soil, they are released, increasing the total ion concentration in the soil solution, thereby increasing electrical conductivity. At the same time, the calcium and magnesium ions released by SS-BC may compete with the heavy metal ions in the soil for cation exchange sites. Due to the moderate ionic radius and charge of calcium and magnesium ions, they are more easily adsorbed by soil colloids, thereby occupying cation exchange sites and leading to a decrease in cation exchange capacity.

Soil volumetric weight is an important indicator reflecting the compactness of soil. Generally, the higher the soil volumetric weight, the denser the soil and the poorer the air permeability. Factors affecting soil volumetric weight mainly include soil organic matter, soil texture, and soil structure. For agricultural land, the soil volumetric weight requirement is typically between 1.1 and 1.4 g/cm^3. From Fig. 4 (D, E), it can be seen that the addition of SS-BC to heavy metal contaminated

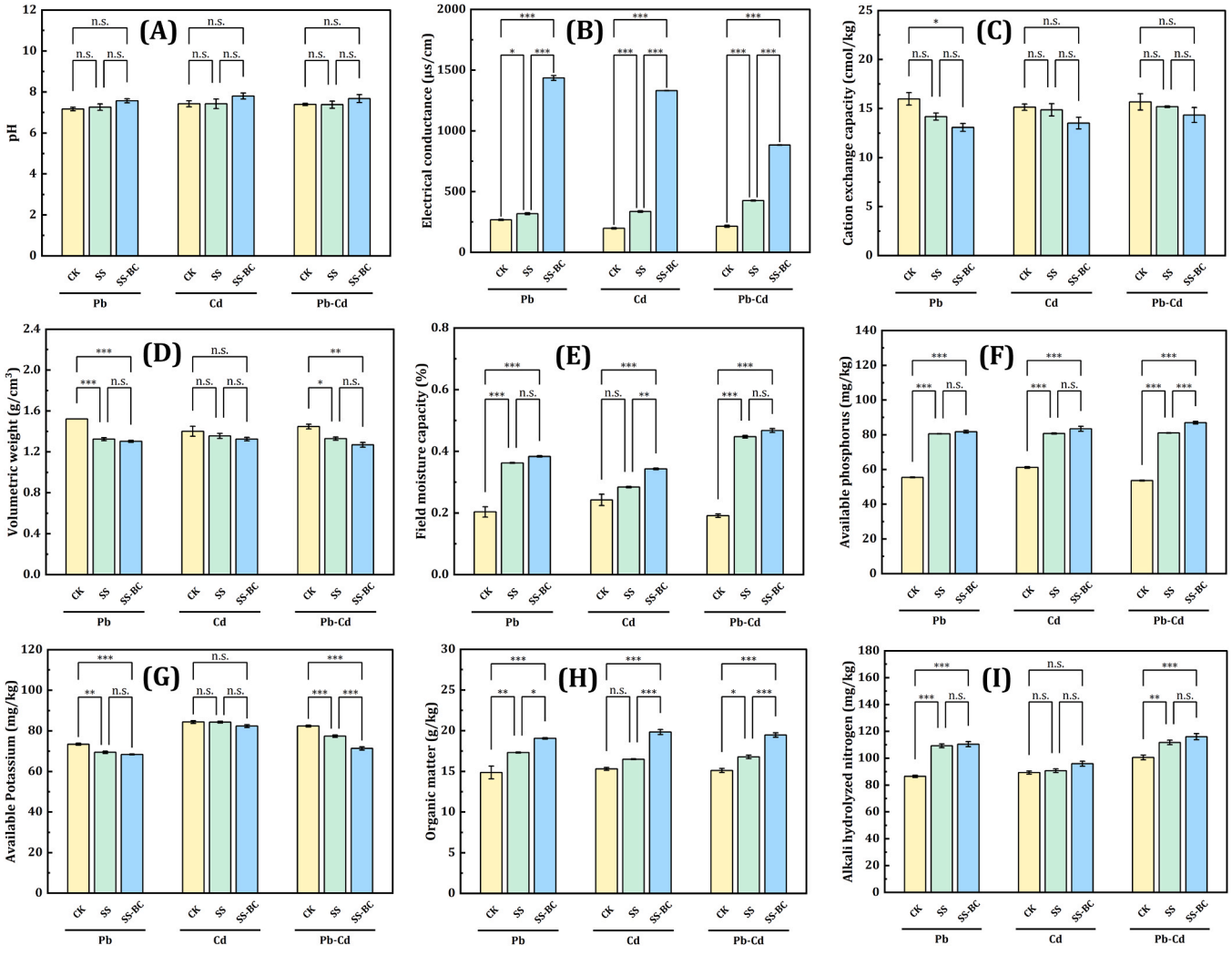

Fig. 4. Physicochemical properties of soil after planting oilseed rape in heavy metal-contaminated soil treated with SS and SS-BC: pH (A), electrical conductivity (B), cation exchange capacity (C), volumetric weight (D), field moisture capacity (E), available phosphorus (F), available potassium (G), organic matter (H), alkali-hydrolyzable nitrogen (I). Where $p \leq 0.05$ is generally significant, denoted as *; $p \leq 0.01$ is significant, denoted as **; $p \leq 0.001$ is highly significant, denoted as ***.

soil decreased the soil's volumetric weight and increased the water holding capacity in the field. The reason for the decrease in soil volumetric weight after the addition of SS-BC is that SS-BC has a high specific surface area and porosity, which allows it to adsorb and retain a large amount of water. After adding SS-BC, the soil's water retention capacity is significantly enhanced. Biochar and modified steel slag can improve the soil's aggregate structure and increase its porosity. A better aggregate structure helps reduce soil compaction, thereby lowering the soil volumetric weight. Field moisture capacity is a crucial indicator in agricultural production for determining whether soil requires irrigation, reflecting the maximum threshold of soil moisture retention. Typically, soil texture, depth of groundwater table, organic matter content, and soil profile structure all affect field moisture capacity. The addition of SS-BC can improve the soil's physical structure, increasing its porosity and aeration. These improvements enhance the soil's water infiltration and retention capacity, allowing it to hold more water after rainfall or irrigation.

The level of available phosphorus determines the nutritional effectiveness of phosphorus fertilizers on plants. As can be seen from Fig. 4 (F), the addition of SS-BC increased the effective phosphorus content of the three types of heavy metal contaminated soils by 26.31 mg/kg, 22.22 mg/kg and 33.30 mg/kg, respectively, compared with the control CK. This is mainly because at low addition levels, the increase in soil pH due to SS inhibits the transformation of phosphorus. Additionally, due to the rich phosphorus content in SS, phosphorus is slowly released into the soil with increasing application rates. The calcium and magnesium elements present in SS can also combine with PO_4^{2-} in the soil, generating soluble phosphate and thus increasing the available phosphorus content in the soil. The silicate minerals in SS have strong adsorption capabilities, providing better fixation of phosphorus in the soil and preventing phosphorus loss. From Fig. 4 (G), it can be observed that in the soil with SS-BC, compared to the control group CK, the content of available potassium decreases with increasing SS-BC addition. This may be because SS is rich in calcium and magnesium ions, which exert antagonistic effects on K^+ in the soil, thereby inhibiting the available potassium in the soil. Fig. 4(H) depicts the changes in organic matter content in soil contaminated with different types of metals after addition of SS-BC. It can be seen that the organic matter content of the soil was significantly increased by the addition of SS-BC, which increased by 4.19 mg/kg, 4.54 mg/kg and 4.36 mg/kg, respectively, compared to CK. This is mainly because SS-BC, as an organic polymer complex, is rich in organic matter content, and its addition results in the slow release of organic matter content in the soil. Additionally, due to the rich functional group structure of SS-BC, it can adsorb and fix beneficial elements such as nitrogen, phosphorus, and potassium in the soil, thereby enhancing soil fertility. The addition of SS-BC is beneficial to microbial life activities in the soil to some extent, providing carbon sources and energy required for their growth processes, thus increasing microbial content. Soil alkali-hydrolyzable nitrogen is the sum of inorganic nitrogen and easily decomposable organic nitrogen in the soil. It is an important indicator reflecting the soil's nitrogen supply capacity and characterizing soil fertility. Plants absorb alkali-hydrolyzable nitrogen from the soil to synthesize proteins and other biomolecules necessary for their growth. Soil alkaline dissolved nitrogen content increased by 23.92 mg/kg,6.527 mg/kg and 15.47 mg/kg respectively as shown in Fig. 4(I). This is mainly because mineralization in the soil promotes the slow release of organic nitrogen contained in SS. Additionally, the action of fine particles in SS increases soil porosity and water retention capacity, further promoting nitrogen supply in the soil. In addition, the biochar-modified steel slag has strong adsorption and ion-exchange capacity, which can adsorb ammonium nitrogen in the soil and convert it to NH_4^+, thus reducing ammonia loss.

3.3.1. The impact of planting rapeseed in soil treated with steel slag modified material on various growth indicators of rapeseed

The yields of oilseed rape grown in different types of heavy metal polluted soils treated with steel slag modified materials are shown in Fig. 5 (A-F). It can be seen that SS-BC treatment of all types of heavy metal contaminated soil significantly increased plant height, fresh weight, dry weight, chlorophyll content and nitrogen content of plants, in which, compared with CK group, the plant height of oilseed rape increased by 58.33 %, 98.21 % and 130.14 %, respectively, and the fresh weight of oilseed rape increased by 157.97 %, 140.98 % and 424.24 %, respectively. It showed that SS-BC had positive effects in reducing heavy metal toxicity and promoting plant growth. Especially, the soil co-polluted with Pb and Cd had a certain inhibitory effect on plant growth, but this inhibitory effect was significantly reduced after adding SS-BC, which has a strong ability to adsorb and fix heavy metal ions. When heavy metal ions are adsorbed or immobilised on soil particles by SS-BC, their direct toxicity to plant roots will be reduced, thus reducing the inhibitory effect of heavy metals on oilseed rape growth. Meanwhile, SS-BC itself contains some nutrient elements that are beneficial to plant growth, such as calcium and silicon. These elements can be absorbed and utilised by oilseed rape after being released in the soil, further promoting the growth of oilseed rape.

3.3.2. The effect of planting rapeseed in soil treated with steel slag modified material on heavy metal content and speciation in soil and rapeseed

Fig. 6 (A) shows the immobilization efficiency of heavy metals in soil contaminated with different types of heavy metals after amending with steel slag and its modified materials and planting rapeseed. It can be seen that the immobilization efficiency of heavy metals Pb and Cd increased by 8.68 % and 23.04 %, respectively, in the soil with single heavy metal contamination after adding SS-BC. In the soil with mixed contamination of Pb and Cd, the immobilization efficiency of heavy metals Pb and Cd increased by 14.43 % and 8.48 %, respectively, after adding SS-BC. The presence of single versus mixed heavy metal contamination can affect the immobilization efficiency. In soils with single metal contamination, the competition for adsorption sites on SS-BC is lower, leading to higher immobilization efficiency for each metal. In contrast, in soils with mixed contamination, Pb and Cd may compete for the same adsorption sites, potentially reducing the efficiency of immobilization for each metal individually. The interactions between Pb and Cd in mixed contamination scenarios might influence their behavior and immobilization in the soil. These interactions can affect how each metal is adsorbed onto the SS-BC, potentially explaining the different efficiencies observed.

Fig. 6 (B, C) shows the heavy metal content in the stems, leaves, and roots of rapeseed plants grown in soils contaminated with different types of heavy metals. It can be seen that in soils contaminated with single heavy metals, the content of heavy metals Pb and Cd in the stems and leaves of rapeseed decreased by 25.96 mg/g and 8.02 mg/g, respectively. This could be due to the limited ability of rapeseed to absorb and translocate heavy metals during growth. Some heavy metals are transferred to the above-ground parts of the plant, but the translocation efficiency is not high, resulting in a smaller decrease in content. In the roots of rapeseed, the content of heavy metals Pb and Cd decreased by 77.73 mg/g and 30.11 mg/g, respectively, indicating that rapeseed more effectively absorbed these heavy metals in single-contaminated soils and primarily accumulated them in the roots. As the main absorbing organ of the plant, the roots are in close contact with the soil and can accumulate more heavy metals. In soils with mixed heavy metal contamination, the content of heavy metals Pb and Cd in the stems and leaves of rapeseed decreased by 39.76 mg/g and 59.94 mg/g, respectively. Compared to single contamination, mixed heavy metal contamination may lead to enhanced stress responses in the plant, activating more translocation mechanisms and transferring more heavy metals to the above-ground parts. The content of heavy metals Pb and Cd in the roots decreased by 59.46 mg/g and 72.17 mg/g, respectively. This indicates that under mixed heavy metal contamination, the rapeseed's ability to absorb heavy metals in the roots is enhanced. However, due to competitive absorption and transport mechanisms, some heavy metals

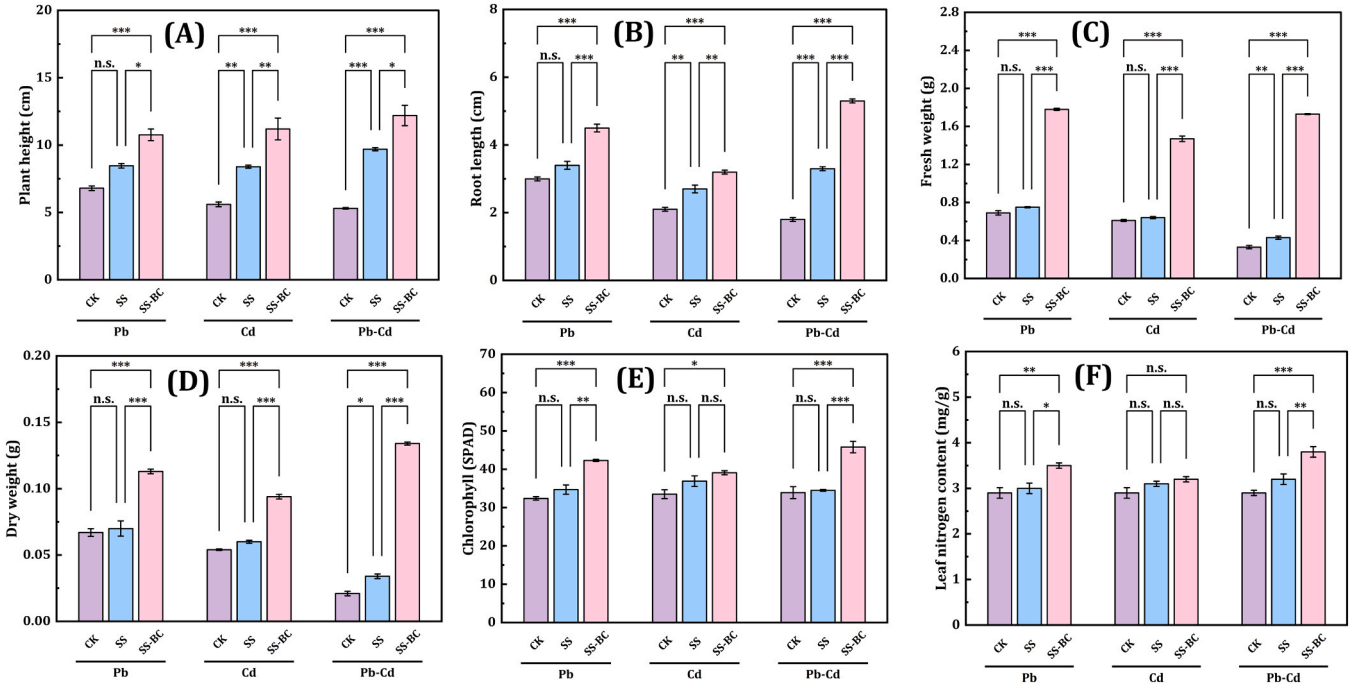

Fig. 5. Growth parameters of oilseed rape plants grown in soil contaminated with different types of heavy metals and treated with steel slag-modified materials: plant height (A), root length (B), fresh weight (C), dry weight (D), chlorophyll content (E), and nitrogen content in leaves (F).

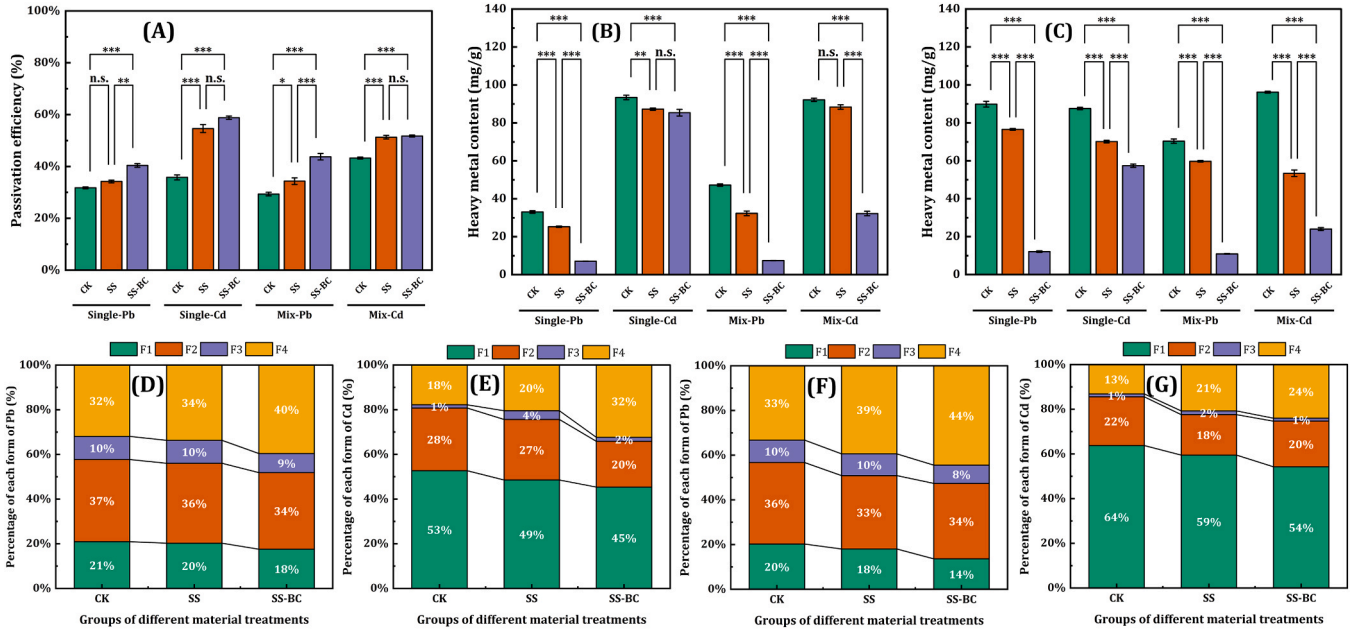

Fig. 6. Immobilization efficiency of various heavy metals in soil treated with steel slag-modified materials and planted with oilseed rape (A), heavy metal content in the stems and leaves of oilseed rape (B), heavy metal content in the roots of oilseed rape (C), distribution of heavy metal forms in soil treated with steel slag-modified materials and planted with oilseed rape in single Pb-contaminated soil (D), distribution of heavy metal forms in soil treated with steel slag-modified materials and planted with oilseed rape in single Cd-contaminated soil (E), distribution of heavy metal forms in soil treated with steel slag-modified materials and planted with oilseed rape in Pb (F) and Cd (G) co-contaminated soil. Where $p \leq 0.05$ is generally significant, denoted as *; $p \leq 0.01$ is significant, denoted as **; $p \leq 0.001$ is highly significant, denoted as ***.

are transferred to the stems and leaves. There may be synergistic or antagonistic effects between different heavy metals, which affect the distribution and accumulation of heavy metals within the plant.

By planting rapeseed and then measuring the heavy metal content in each part, the transfer factor (TF) and bioaccumulation factor (BAF) of the heavy metals are calculated [56]. The calculation formulas are as follows:

$$TF = \frac{C_L}{C_R} \tag{5}$$

$$BAF = \frac{C_L}{C_0} \tag{6}$$

Where C_L refers to the heavy metal content in the stems and leaves of the rapeseed, measured in mg/g; C_R refers to the heavy metal content in the roots of the rapeseed, measured in mg/g; and C_0 refers to the initial heavy metal content in the soil, measured in mg/kg.

The Bioconcentration Factor (BAF) evaluates the ability of Oilseed Rape to absorb and accumulate lead from the soil; a higher BAF value indicates a stronger ability to absorb and accumulate lead. The Translocation Factor (TF) is used to describe the ability of Oilseed Rape to transport lead from the roots to the above-ground parts; a higher TF value indicates a stronger translocation ability. By combining the TF and BAF values from Table 4, a further analysis of rapeseed performance in soils with single and mixed heavy metal contamination can provide a deeper understanding of its mechanisms for heavy metal uptake and distribution. For single heavy metal Pb contamination, under CK and SS treatments, the TF and BAF values in the leaves and roots show little difference, indicating the limited ability of rapeseed to absorb and translocate Pb. Under SS-BC treatment, TF significantly increased to 0.59 and BAF significantly decreased to 0.01 and 0.02 in leaves and roots, respectively. This suggests that the addition of biochar significantly inhibits the accumulation of Pb in the roots and promotes its translocation to the leaves. For single heavy metal Cd contamination, rapeseed shows a strong ability to absorb and translocate Cd, especially under SS and SS-BC treatments, where the TF in the leaves significantly increases to 1.24 and 1.49, respectively. However, the BAF values show a decreasing trend with treatment, particularly under the SS-BC treatment, where the BAF decreases to 0.57. This may be due to the addition of SS-BC altering the bioavailability of Cd, enhancing absorption by the leaves while reducing accumulation in the roots.

In soils with mixed heavy metal contamination, the parameters for heavy metal Pb indicate that the TF in the leaves does not vary much across treatments, but the TF and BAF in the roots significantly decrease to 0.03 and 0.04 under the SS-BC treatment. This suggests that biochar more effectively inhibits the accumulation of Pb in the roots and promotes its translocation to the leaves under mixed Pb contamination, similar to the single Pb contamination scenario. For heavy metal Cd in mixed contamination, the parameters indicate that the TF and BAF in the roots are higher under CK and SS treatments, especially in the CK treatment, showing high accumulation of Cd in the roots. Under the SS-BC treatment, the TF in the leaves is higher (1.19), but the TF and BAF in the roots significantly decrease to 0.64 and 0.54, respectively. This indicates that biochar similarly inhibits the accumulation of Cd in the roots and promotes its translocation to the leaves under mixed Cd contamination.

Fig. 5(D-G) show the distribution of heavy metal forms in soils with single and mixed heavy metal contamination. It can be seen that SS-BC significantly reduces the content of exchangeable Pb and Cd and significantly increases the content of residual Pb and Cd. This indicates that biochar-modified steel slag can immobilize Pb and Cd. SS-BC alters the chemical forms of the heavy metals, making them more stable, thereby effectively reducing the harm of heavy metal pollution to rapeseed and the soil ecosystem. By combining the ecological risk factor values from Table 5, we can further analyze the performance of rapeseed in soils with single and mixed heavy metal contamination and explore its impact on heavy metal uptake and ecological risk. In soils with single heavy metal contamination, the MF values of Pb and Cd further decrease to 17.56 and 45.36, respectively, and the Cf and Er values also significantly decrease. This indicates that the SS-BC treatment has a significant effect on immobilizing Pb and Cd, reducing their accumulation in the soil and their ecological risks. Similarly, in soils with mixed heavy metal contamination, the MF values of Pb and Cd significantly decrease to 13.60 and 54.24, respectively, and the C_f and E_r values also significantly decrease. This shows that SS-BC treatment more effectively reduces the accumulation and ecological risks of heavy metals under mixed Pb and Cd contamination. The addition of SS-BC may reduce the bioavailability of heavy metals by altering their chemical forms and enhancing their immobilization, thereby effectively mitigating the harm of heavy metal pollution to rapeseed and the soil ecosystem.

3.3.3. Correlation analysis and principal component analysis

To further investigate the relationship between the forms of heavy metals in the soil, the physicochemical properties, and plant growth, a correlation analysis was conducted on various physicochemical indicators in the plant-soil system. As shown in Fig. 7 (A-C), the passivation efficiency of heavy metals in soils contaminated with three types of heavy metals was significantly positively correlated with plant growth indicators such as fresh weight, dry weight, plant height, and root length. Meanwhile, the effective state content of heavy metals in plants was significantly negatively correlated with various plant growth indicators. This indicates that the addition of steel slag-modified materials to the soil improves the passivation efficiency of heavy metals, immobilizes heavy metals in the soil, and converts them into less mobile residue states. Consequently, the transfer of heavy metals to plants is reduced, lowering their toxicity and promoting plant growth. The organic matter content in the soil was positively correlated with the passivation efficiency of heavy metals, suggesting that the introduction of biochar increases soil organic matter content and that soil organic matter has a certain passivation effect on heavy metals.

The principal component analysis (PCA) of the physicochemical indicators of soils contaminated with different types of heavy metals and the various plant growth indicators is shown in Fig. 7 (D-F). The variance contribution rate of principal component 1 and principal component 2 reached 81.60 %, indicating that the relationship between soil physicochemical properties and plant growth indicators can be approximately explained by the two principal components. As shown in the figure, the passivation efficiency of heavy metals in the soil is negatively correlated with the effective state content of heavy metals in plants, indicating that heavy metals in the soil inhibit plant growth. Meanwhile, soil alkaline nitrogen, available phosphorus, and rapidly

Table 4
Effect of steel slag modified materials on the uptake and translocation of lead and cadmium in small oilseed rape.

Contamination type	Treatment	TF	BAF	
			Leave	Root
single Pb	CK	0.37	0.07	0.18
	SS	0.33	0.05	0.15
	SS-BC	0.59	0.01	0.02
single Cd	CK	1.07	0.93	0.88
	SS	1.24	0.87	0.70
	SS-BC	1.49	0.85	0.57
Mix Pb	CK	0.67	0.19	0.28
	SS	0.54	0.13	0.24
	SS-BC	0.68	0.03	0.04
Mix Cd	CK	0.96	1.84	1.92
	SS	1.60	1.77	1.10
	SS-BC	1.19	0.64	0.54

Table 5
Pollution factors and risk indices of different types of contaminated soils after potting experiments.

Contamination type	Treatment	MF	C_f	E_r	RI (SS-BC)
single Pb	CK	20.92	2.13	10.66	7.62
	SS	20.25	1.96	9.84	
	SS-BC	17.56	1.52	7.62	
single Cd	CK	52.68	4.60	23.04	10.44
	SS	48.52	3.88	19.42	
	SS-BC	45.36	2.08	10.44	
Mix Pb	CK	20.21	2.01	60.19	132.46
	SS	18.01	1.53	46.10	
	SS-BC	13.60	1.24	37.46	
Mix Cd	CK	63.74	6.59	197.96	
	SS	59.48	3.81	114.50	
	SS-BC	54.24	3.16	95.00	

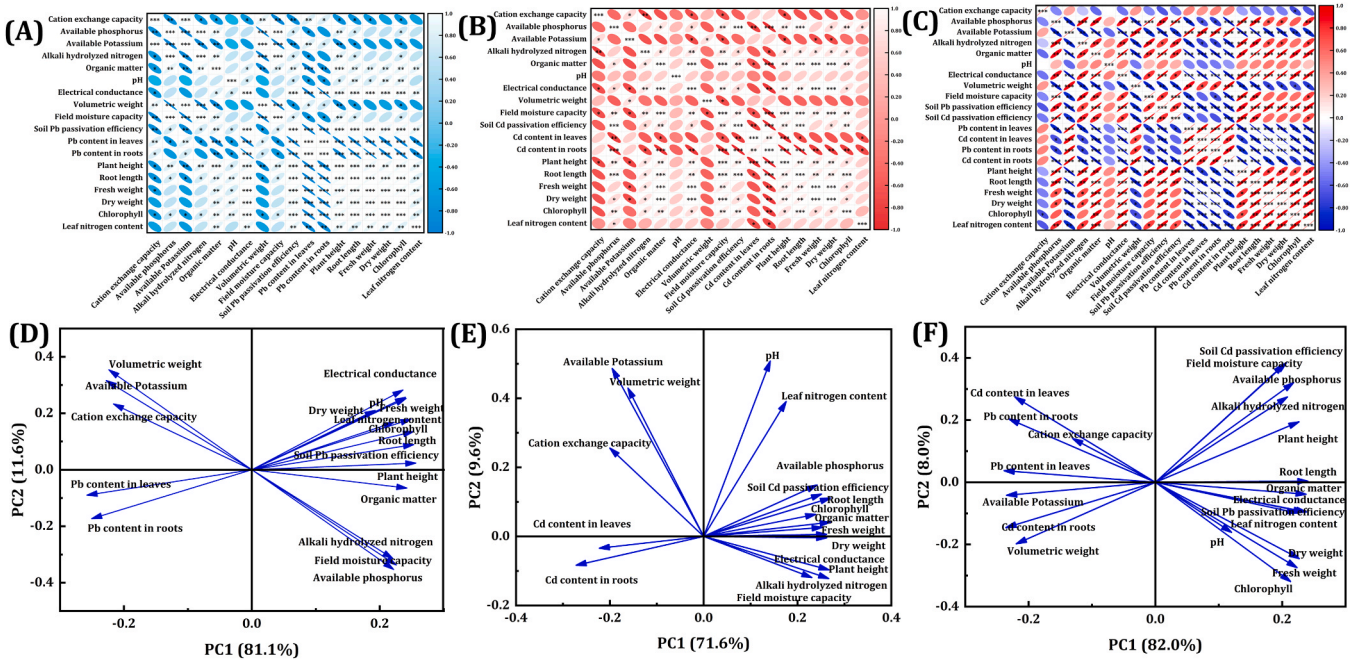

Fig. 7. Correlation analysis of each physico-chemical indicator for single Pb-polluted soil, single Cd-polluted and mixed Pb and Cd-polluted soil; principal component analysis of each physico-chemical indicator for single Pb-polluted soil, single Cd-polluted and mixed Pb and Cd-polluted soil.

available potassium are positively correlated with various plant physiological indicators, consistent with the correlation analysis conclusion discussed above, indicating that nutrients such as nitrogen, phosphorus, and potassium in the soil can promote plant growth.

The correlation matrix and loading matrix of the principal component analysis are shown in Table 6. The elements in the loading matrix represent the contribution to the corresponding principal component; the larger the absolute value, the greater the contribution of that element to the principal component. It can be seen that in the loading matrix of principal component 1, the load values of soil heavy metal passivation efficiency and the effective state content of heavy metals in plants are relatively high, indicating that principal component 1 mainly contributes to the passivation efficiency of soil heavy metals and the effective state content of heavy metals in plants. In contrast, in the loading matrix of principal component 2, the load values of soil available phosphorus, pH, field capacity, etc., are relatively high, indicating that principal component 2 mainly contributes to the physicochemical indicators of the soil.

3.4. Evaluation of ecological and economic benefits

Leaching toxicity refers to the property of solid waste where harmful substances transfer into water during contact, polluting the environment and endangering human health. By identifying the leaching toxicity concentration of solid waste, it is determined whether the substance is hazardous waste with leaching toxicity. Steel slag, a product of industrial solid waste, mainly contains heavy metals as harmful components. Leaching toxicity tests on steel slag are conducted to evaluate whether

Table 6
Principal component loading matrix.

Types of heavy metal pollution	single Pb		single Cd		Mix Pb-Cd	
Soil physical and chemical indicators	PC1	PC2	PC1	PC2	PC1	PC2
Cation exchange capacity	−0.2164	0.2330	−0.1999	0.2559	−0.1306	0.1406
Available phosphorus	0.2216	−0.3530	0.2418	0.1487	0.2180	0.3205
Available Potassium	−0.2277	0.3160	−0.1949	0.4867	−0.2350	−0.0420
Alkali hydrolyzed nitrogen	0.2207	−0.3147	0.2307	−0.1192	0.2083	0.2745
Organic matter	0.2425	−0.0648	0.2698	0.0410	0.2377	−0.0386
pH	0.1928	0.2103	0.1419	0.5078	0.1202	−0.1611
Electrical conductance	0.2402	0.2567	0.2622	−0.0041	0.2385	−0.0956
Volumetric weight	−0.2235	0.3539	−0.1614	0.4294	−0.2196	−0.1981
Field moisture capacity	0.2257	−0.3374	0.2665	−0.1219	0.2067	0.3842
Soil Pb passivation efficiency	0.2532	0.089	/	/	0.2345	−0.0952
Soil Cd passivation efficiency	/	/	0.2511	0.1224	0.2026	0.3788
Pb content in leaves	−0.2579	−0.0897	/	/	−0.2388	0.0371
Cd content in leaves	/	/	−0.2223	−0.0341	−0.2216	0.2738
Pb content in roots	−0.2505	−0.1735	/	/	−0.2311	0.2035
Cd content in roots	/	/	−0.2719	−0.0836	−0.2360	−0.1458
Plant height	0.2565	0.0235	0.2671	−0.0968	0.2266	0.1944
Root length	0.2530	0.1350	0.2703	0.1111	0.2406	0.0037
Fresh weight	0.2412	0.2525	0.2526	0.0259	0.2234	−0.2744
Dry weight	0.2363	0.2823	0.2621	0.0061	0.2269	−0.2454
Chlorophyll	0.2488	0.1790	0.2388	0.0638	0.2134	−0.3192
Leaf nitrogen content	0.2223	0.1679	0.1758	0.3906	0.2239	−0.0989

the heavy metal content exceeds the standard. The test results are shown in Table 7.

The leaching toxicity tests on steel slag from Chongqing Steel Plant were conducted using the "Leaching Method for Toxicity Identification of Solid Waste" (GB5086.1–1997). The test measured heavy metal indicators Hg, Pb, As, Cd, Cr, Cu, Zn, and Ni. According to the concentration limits of hazardous components in leachate specified in the "Identification Standards for Hazardous Waste - Identification of Leaching Toxicity" (GB 5086.3–2007), the heavy metal content in steel slag did not exceed the hazardous waste standard values and met the "Soil Environmental Quality Standards" (GB 15618–1995). Therefore, steel slag can be used as an agricultural amendment (All the above standards are from the AQSIQ of the People's Republic of China).

Table 7
Steel slag leaching toxicity results.

Metal indicators	Detection value (mg/kg)	Standard value (mg/kg)
Hg	0.003	0.10
Pb	0.006	5.00
As	0.018	1.50
Cd	0.000	1.00
Cr	0.505	15.00
Cu	0.011	100.00
Zn	0.014	100.00
Ni	0.000	5.00

4. Conclusions and prospects

This study investigated the use of SS-BC as a heavy metal passivator for the remediation of soils contaminated with various heavy metals. The results demonstrated that the addition of SS-BC not only improved soil fertility but also significantly reduced the bioavailable concentrations of heavy metals in the soil. The passivation efficiencies for Pb and Cd were 51.76 % and 63.74 %, respectively. Moreover, in soils contaminated with different types of heavy metals, the application of SS-BC led to a transformation of heavy metals into more stable residual forms, reduced the acid-extractable fractions, and increased the stability of heavy metals in the soil, thereby decreasing their mobility and bioavailability. After treating heavy metal-contaminated soils with SS-BC, there were significant improvements in plant height, fresh weight, dry weight, chlorophyll content, and nitrogen content. A simulated indoor cultivation of rapeseed revealed that the addition of SS-BC significantly lowered the heavy metal content in the plants, suppressed the accumulation of heavy metals in the roots, and reduced their translocation to the leaves. The use of SS-BC in contaminated soils enhanced biological activity and crop yield by immobilizing and transforming heavy metals, improving soil properties, and releasing nutrients. In summary, SS-BC is an effective soil passivator that can significantly reduce the toxicity and bioavailability of Pb and Cd in contaminated soils, making it a promising soil amendment and heavy metal passivator. Future research could explore the effectiveness of SS-BC in different types of heavy metal contaminated soils, such as for soil environments with multiple heavy metal contamination or coexisting with organic pollutants. Meanwhile, the effect of SS-BC in combination with other soil amendments could be further investigated to improve treatment efficiency and stability. The current study mainly focuses on laboratory and potting experiments, and in the future, large-scale application trials can be conducted under actual field conditions to verify the effectiveness of SS-BC in different soil types and environmental conditions. Meanwhile, long-term monitoring and evaluation of the passivation effect and stability of SS-BC is necessary, especially the performance during multiple cropping seasons.

CRediT authorship contribution statement

An Wang: Writing – original draft, Methodology, Investigation, Data curation. **Yifan Liu:** Investigation. **Jie Ren:** Investigation, Data curation. **Yang Zeng:** Methodology. **Zhanbin Huang:** Writing – original draft, Investigation. **Ying Zhang:** Data curation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

This work was financially supported by the Fundamental Research Funds for the Central Universities (Ph.D. Top Innovative Talents Fund of CUMTB) (BBJ2024053), and the Research on the Application of Ecological Remediation of Legacy Steel Slag in Contaminated Land (CCEED-2022-4-07) and the partner company, CSCEC 8TH Division Environmental Technology Co., Ltd, Shanghai.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2024.114026.

References

[1] A.A. Basaleh, et al., Poly(acrylamide acrylic acid) grafted on steel slag as an efficient magnetic adsorbent for cationic and anionic dyes, J. Environ. Chem. Eng. 9 (2021) 105126.
[2] W. Cao, et al., Adsorption and migration behaviors of heavy metals (As, Cd, and Cr) in single and binary systems in typical Chinese soils, Sci. Total Environ. 950 (2024) 175253.
[3] H. Chen, et al., Assessing simultaneous immobilization of lead and improvement of phosphorus availability through application of phosphorus-rich biochar in a contaminated soil: a pot experiment, Chemosphere 296 (2022) 133891.
[4] L. Chen, et al., Passivation of heavy metals during co-composting of Camellia oleifera by-products and river sediment with the additives of MnO2-loaded biochar, Ind. Crops Prod. 215 (2024) 118697.
[5] T. Chen, et al., Study on the solidification/stabilization of cadmium-contaminated soil by red mud-assisted blast furnace slag under excitation conditions, J. Clean. Prod. 435 (2024) 140505.
[6] F.P. Dad, et al., Adsorption of trace heavy metals through organic compounds enriched biochar using isotherm adsorption and kinetic models, Environ. Res. 241 (2024) 117702.
[7] P. Devi, et al., Stabilization and solidification of arsenic and iron contaminated canola meal biochar using chemically modified phosphate binders, J. Hazard. Mater. 385 (2020) 121559.
[8] Y. Du, et al., Exploring the accumulation capacity of dominant plants based on soil heavy metals forms and assessing heavy metals contamination characteristics near gold tailings ponds, J. Environ. Manag. 351 (2024) 119838.
[9] C. Fang, et al., Magnetic recyclable Co-MOF derivate-modified steel slag for tetracycline removal by integrated adsorption and Fenton-like catalysis, J. Water Process Eng. 63 (2024) 105434.
[10] L. Hakanson, An ecological risk index for aquatic pollution control.a sedimentological approach, Water Res. 14 (1980) 975–1001.
[11] C. He, et al., Phytoremediation of soil heavy metals (Cd and Zn) by castor seedlings: tolerance, accumulation and subcellular distribution, Chemosphere 252 (2020) 126471.
[12] J. Jiang, et al., Immobilization of Cu(II), Pb(II) and Cd(II) by the addition of rice straw derived biochar to a simulated polluted Ultisol, J. Hazard. Mater. 229-230 (2012) 145–150.
[13] Q. Jiang, et al., Solidification/stabilization of soil heavy metals by alkaline industrial wastes: a critical review, Environ. Pollut. 312 (2022) 120094.
[14] M. Jiaying, et al., Functions of nitrogen, phosphorus and potassium in energy status and their influences on rice growth and development, Rice Sci. 29 (2022) 166–178.
[15] N. Karami, et al., Efficiency of green waste compost and biochar soil amendments for reducing lead and copper mobility and uptake to ryegrass, J. Hazard. Mater. 191 (2011) 41–48.
[16] W. Lan, et al., Research progress of biochar modification technology and its application in environmental remediation, Biomass Bioenergy 184 (2024) 107178.

[17] J. Li, et al., Soil fertility and heavy metal pollution (Pb and Cd) alter kin interaction of Sorghum vulgare, Environ. Exp. Bot. 155 (2018) 368–377.
[18] X. Li, et al., Combined toxicity and detoxification of lead, cadmium and arsenic in Solanum nigrum L, J. Hazard. Mater. 389 (2020) 121874.
[19] X. Li, et al., Sb/As immobilization and soil function improvement under the combined remediation strategy of modified biochar and Sb-oxidizing bacteria at a smelting site, J. Hazard. Mater. 471 (2024) 134302.
[20] Y. Li, et al., Effects of α-Fe2O3 modified chicken manure biochar on the availability of multiple heavy metals and soil biochemical properties, J. Environ. Chem. Eng. 11 (2023) 109922.
[21] Y. Luo, et al., Vertical migration behavior simulation and prediction of Pb and Cd in co-contaminated soil around Pb-Zn smelting slag site, J. Hazard. Mater. 469 (2024) 133990.
[22] Z. Malone, et al., Impacts of organic matter amendments on urban soil carbon and soil quality: a meta-analysis, J. Clean. Prod. 419 (2023) 138148.
[23] S. Mao, et al., Heavy metal pollution pressure in gold mines shows overall suppressed biochemical sulfur cycle, Int. Biodeterior. Biodegrad. 191 (2024) 105807.
[24] W. Mao, et al., Synergistic adsorption removal of heavy metal oxoanions and cations from aqueous solution by a polyacrylate-coated ferrous sulfide and layered double hydroxide nanocomposite, Chem. Eng. J. 487 (2024) 150518.
[25] S. Mingming, et al., The adsorption properties of steel slag-based porous geopolymer for Cu2+ removal, Miner. Eng. 201 (2023) 108225.
[26] A. Moureen, et al., Untapped potential of food waste derived biochar for the removal of heavy metals from wastewater, Chemosphere 356 (2024) 141932.
[27] L.P. Padhye, et al., Contaminant containment for sustainable remediation of persistent contaminants in soil and groundwater, J. Hazard. Mater. 455 (2023) 131575.
[28] H.K. Pathak, et al., Recent advancement of nano-biochar for the remediation of heavy metals and emerging contaminants: mechanism, adsorption kinetic model, plant growth and development, Environ. Res. 255 (2024) 119136.
[29] Z. Ren, et al., Solidification/stabilization of lead-contaminated soils by phosphogypsum slag-based cementitious materials, Sci. Total Environ. 857 (2023) 159552.
[30] Z. Ren, et al., Stabilization and solidification mechanism of Pb in phosphogypsum slag-based cementitious materials, Constr. Build. Mater. 368 (2023) 130427.
[31] S. Shao, et al., Research on efficient removal of ciprofloxacin through sequential rice straw biochar modification via alkali activation and manganese oxides, Environ. Technol. Innov. 34 (2024) 103611.
[32] X. Shen, et al., Phytoavailability of Cd and Pb in crop straw biochar-amended soil is related to the heavy metal content of both biochar and soil, J. Environ. Manag. 168 (2016) 245–251.
[33] C. Shi, et al., Mechanism, application, influencing factors and environmental benefit assessment of steel slag in removing pollutants from water: a review, J. Water Process Eng. 47 (2022) 102666.
[34] J.-Z. Su, et al., Preparation and applications of iron/biochar composites in remediation of heavy metal contaminated soils: Current status and further perspectives, Environ. Technol. Innov. 35 (2024) 103671.
[35] A. Wang, et al., Effects of composite environmental materials on the passivation and biochemical effectiveness of Pb and Cd in soil: analyses at the ex-planta of the Pak-choi root and leave, Environ. Pollut. 309 (2022) 119812.
[36] A. Wang, et al., Experimental and mechanistic study on the removal of lead from solution by sulfuric acid modified steel slag adsorbent, J. Environ. Chem. Eng. 11 (2023) 111134.
[37] A. Wang, et al., Utilizing different types of biomass materials to modify steel slag for the preparation of composite materials used in the adsorption and solidification of Pb in solutions and soil, Sci. Total Environ. 914 (2024) 170023.
[38] K. Wang, et al., The amelioration and improvement effects of modified biochar derived from Spartina alterniflora on coastal wetland soil and Suaeda salsa growth, Environ. Res. 240 (2024) 117426.
[39] L. Wang, et al., Steel slag as a cost-effective adsorbent for synergic removal of collectors, Cu(II) and Pb(II) ions from flotation wastewaters, Miner. Eng. 183 (2022) 107593.
[40] L. Wang, et al., Green remediation of Cd and Hg contaminated soil using humic acid modified montmorillonite: immobilization performance under accelerated ageing conditions, J. Hazard. Mater. 387 (2020) 122005.
[41] M. Wang, et al., Treatment of Cd(II) and As(V) co-contamination in aqueous environment by steel slag-biochar composites and its mechanism, J. Hazard. Mater. 447 (2023) 130784.
[42] P. Wang, et al., Preparation of two types plant biochars and application in soil quality improvement, Sci. Total Environ. 906 (2024) 167334.
[43] X. Wang, et al., Study on the effects of new developed biochar and sludge composite materials on copper and lead contaminated soil and its remediation mechanism, Environ. Technol. Innov. 32 (2023) 103429.
[44] Y. Wang, et al., Stabilization of Hg2+ and Pb2+ in soil using humic acid residue modified by NH4H2PO4, J. Mol. Struct. 1282 (2023) 135250.
[45] N. Xie, et al., Assessment of the variation of heavy metal pollutants in soil and crop plants through field and laboratory tests, Sci. Total Environ. 811 (2022) 152343.
[46] S.M. Yahaya, et al., Recent advances in the chemistry of nitrogen, phosphorus and potassium as fertilizers in soil: a review, Pedosphere 33 (2023) 385–406.
[47] S. Yang, et al., Insights into remediation of cadmium and lead contaminated-soil by Fe-Mn modified biochar, J. Environ. Chem. Eng. 12 (2024) 112771.
[48] Z. Yang, et al., Research progress on remediation of heavy metal contaminated soil by electrokinetic-permeable reactive barrier, Chem. Eng. J. 490 (2024) 151548.
[49] C. Yao, et al., Heavy metal pollution in agricultural soils from surrounding industries with low emissions: assessing contamination levels and sources, Sci. Total Environ. 917 (2024) 170610.
[50] Z. Yin, et al., Bioaccumulation and transferreing for impacts on Cd and Pb by aphid consumption of the broad bean, Vicia faba L, in soil heavy metal pollution, Chemosphere 360 (2024) 142429.
[51] S. Yu, et al., A review on recent advances of biochar from agricultural and forestry wastes: preparation, modification and applications in wastewater treatment, J. Environ. Chem. Eng. 12 (2024) 111638.
[52] Y.-q Yu, et al., Effectiveness, stabilization, and potential feasible analysis of a biochar material on simultaneous remediation and quality improvement of vanadium contaminated soil, J. Clean. Prod. 277 (2020) 123506.
[53] J. Yuan, et al., Biochar derived from traditional Chinese medicine residues: an efficient adsorbent for heavy metal Pb(II), Arab. J. Chem. 17 (2024) 105606.
[54] F. Zeng, et al., The influence of pH and organic matter content in paddy soil on heavy metal availability and their uptake by rice plants, Environ. Pollut. 159 (2011) 84–91.
[55] S. Zhang, et al., Soil organic matter degradation and methylmercury dynamics in Hg-contaminated soils: relationships and driving factors, J. Environ. Manag. 356 (2024) 120432.
[56] P. Zhao, et al., Two recyclable and complementary adsorbents of coal-based and bio-based humic acids: high efficient adsorption and immobilization remediation for Pb(II) contaminated water and soil, Chemosphere 318 (2023) 137963.
[57] Z. Zhu, et al., Effect of aluminosilicates on the release and form transformation of semi-volatile heavy metals during the combustion of hyperaccumulator plants, J. Clean. Prod. 461 (2024) 142604.